



Degradation of emerging concern contaminants in water by heterogeneous photocatalysis with $\text{Na}_4\text{W}_{10}\text{O}_{32}$



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ABSTRACT

Contaminants of emerging concern (CECs), including pharmaceuticals, are frequently detected at low concentrations in natural water and can cause adverse effect in biota, such as antibiotic resistance. Therefore, it is important to reduce their introduction in the environment by increasing their removal efficiency from wastewaters. In this work, a new photocatalytic method for removal of three CECs target molecules (i.e. atenolol, levofloxacin, trimethoprim) from water is proposed. The photoactive species is decatungstate anion both in solution and immobilized on modified silica particles. The degradation process is studied at ambient temperature, atmospheric pressure and at pH values similar to that of natural waters. EPR spin trapping technique and HPLC–MS analysis give evidence that degradation is mediated by OH^\bullet radicals. The heterogeneous catalyst is stable and can be recycled without a significant loss of efficiency thus opening the possibility of developing new solid materials with interesting photocatalytic performance.

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1. Introduction

Water pollution is a severe worldwide problem whose solution requires new concepts to implement wastewater treatment plants (WWTPs). In fact, a large variety of substances, among them pharmaceuticals [1,2], are not completely removed by the tertiary treatment of urban wastewater plant [3]. Their presence in natural and drinking water is of public health concern [4,5], for the potential effects associated with long term ingestion of mixtures of these compounds even at very low concentration level [6]. Thus, effective removal of pharmaceuticals and other pollutants from wastewaters before their discharge [7] into the environment is an ever pressing requirement.

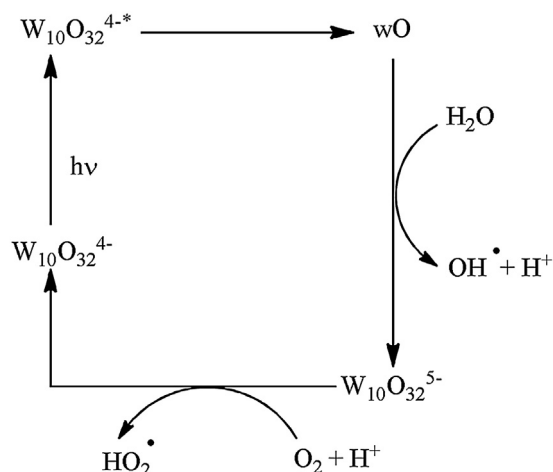
Among the oxidative methodologies proposed to improve the decontamination process, heterogeneous photocatalysis using TiO_2 is by far the most studied method for water purification and several publications and reviews exist on the subject [8–15]. Usually, its action adds to direct photolysis of drug molecules, and results open the possibility to carry out new applications by using also other heterogeneous photocatalysts. For instance, it has been reported that decatungstate anion ($\text{W}_{10}\text{O}_{32}^{4-}$) is able to mineralize organic pollutants [16–18] in certain experimental conditions, resulting even more efficient than TiO_2 itself. More in detail, $\text{W}_{10}\text{O}_{32}^{4-}$ is

constituted by tungsten and oxygen clusters and it has been widely studied in photocatalysis [19–24] for oxidative processes of interest in fine chemistry. Its absorption spectrum ($\lambda_{\text{max}} = 323 \text{ nm}$) overlaps that of TiO_2 and for this reason it is called a “soluble model” of this semiconducting oxide [25–27]. It has been recently demonstrated by some of us [28] that photoexcitation of aqueous solutions of dissolved $\text{Na}_4\text{W}_{10}\text{O}_{32}$ leads to the formation of OH^\bullet radicals. The proposed mechanism in water is summarized in Scheme 1: the formation of the very reactive transient WO occurs after photoexcitation of $\text{Na}_4\text{W}_{10}\text{O}_{32}$. Then, reaction between WO and water produces OH^\bullet radicals and $\text{W}_{10}\text{O}_{32}^{5-}$ which, in turn, is re-oxidized by O_2 leading again the starting $\text{W}_{10}\text{O}_{32}^{4-}$.

These findings are particularly relevant since OH^\bullet radicals are powerful oxidants, capable of attacking any kind of organic molecule. Therefore, photoexcitation of decatungstate in water represents a remediation method that operates under environmentally friendly conditions (ambient temperature, atmospheric air pressure). Based on this evidence, we investigate the photocatalytic action of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ for the degradation of pharmaceuticals in aqueous matrix. To accomplish this task, three target molecules have been chosen: atenolol (ATN), levofloxacin (LEVO), and trimethoprim (TMP) (Table 1). ATN (a beta-blocker) is hardly biotransformed and it is not efficiently removed by conventional wastewater treatments [29,30]. A recent ecotoxicological study reports that β -blockers affect the aquatic organisms [31]. LEVO and TMP belong to the class of antibiotics. Although TMP is extensively used in human and veterinary medicines, it is poorly absorbed

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Scheme 1. Photocatalytic behaviour of $\text{W}_{10}\text{O}_{32}^{4-}$ in water upon aerobic conditions.

Table 1
Some chemical-physical parameters of the employed drugs.

Drug	Structure	MW	pK _a [20]	logK _{ow} ^a	λ _{max} (nm)
TMP		290.3	3.2 6.7	0.91	203
LEVO		361.4	5.4 8.0	0.63	292
ATN		266.3	9.6	0.17	225

^a Logarithm of the octanol/water partition coefficient.

and metabolized by humans and animals [32]. Additionally, TMP residues cannot be sufficiently removed in WWTPs [33]. LEVO (a fluoroquinolone antibiotic) is a high consumption drug for humans [34], but its removal efficiency in conventional WWTPs is roughly 40% and its presence and activity in wastewater effluents and aquatic environment has been reported [35].

Herein, we report for the first time that photoexcited sodium decatungstate ($\text{Na}_4\text{W}_{10}\text{O}_{32}$) is efficient in the degradation of ATN, LEVO and TMP. However, the applicability of decatungstate in water remediation can be limited from its high solubility that makes difficult to recover it from aqueous solutions. This constraint can be overcome by immobilizing the decatungstate on a solid matrix. Indeed, several successful strategies have been followed based on impregnation [36], entrapment into a silica matrix [37], electrostatic interaction [38,39]. For this reason, we investigated the photocatalytic activity of the polyanion after immobilization on modified silica particles. ESR spin-trapping technique and HPLC–MS analysis are used to elucidate the starting oxidative degradation mechanism and the nature of reaction intermediates. Stability and reuse of the employed heterogeneous photocatalyst are also investigated.

2. Experimental

2.1. Materials

Levofloxacin (LEVO, purity 99.8%), atenolol (ATN, purity 99.8%), trimethoprim (TMP, purity 99.8%) and formic acid were purchased from Fluka (Fluka Chemie AG, Switzerland). Sodium hydroxide (Tiolchimica, Rovigo, Italy), hydrochloric acid (Carlo Erba, Milano,

Italy) of analytical grade were employed to adjust the pH of diluted drugs solutions. The pH was measured using an AMEL pHmeter (Milano, Italy). High-performance liquid chromatography (HPLC) grade acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany). The water was Milli-Q[®] grade (Millipore, MA, USA).

2.2. Photocatalyst preparation

Sodium decatungstate ($\text{Na}_4\text{W}_{10}\text{O}_{32}$) was synthesized following a reported literature procedure [40]. The heterogeneous photocatalyst (silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$) has been prepared suspending the commercial silica gel functionalized with 3-aminopropyl groups (Sigma Aldrich, 1 g) in an aqueous solution (50 mL) of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($8.5 \cdot 10^{-4}$ M, pH = 5.2). At pH 5.2 some of the surface aminic groups are protonated and able to immobilize decatungstate anion by an ionic exchange mechanism. The suspension was stirred for 15 min. Then, the amount of decatungstate attached to the surface was evaluated by the absorbance decrease at 323 nm observed recording UV–vis spectra (spectrophotometer Jasco V570) of the starting solution and of that after the contact with silica gel. The described procedure was repeated suspending again the recovered silica gel in a fresh decatungstate solution until any absorbance decrease was observed. Usually, 5–6 repetitions were necessary. Finally, the solid photocatalyst was dried at 40 °C overnight. From the absorbance decreases, we estimated that the amount of decatungstate immobilized was $177 \mu\text{mol g}^{-1}$.

2.3. Photocatalytic experiments with homogeneous $\text{Na}_4\text{W}_{10}\text{O}_{32}$

An aqueous aerated solution (3 mL, final pH = 6) containing dissolved $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \cdot 10^{-4}$ M) and the drug of interest (10 mg L^{-1}) was put into a quartz spectrophotometric cell (optical path 1 cm) and placed in front of a Hg medium pressure lamp (Helios Italquartz, 15 W cm^{-2}). The solution is magnetically stirred and irradiation was carried out using a cut-off filter, placed between the lamp slit (1 cm × 3 cm) and the cuvette in order to select the suitable wavelength range ($\lambda > 300 \text{ nm}$ for ATN and TMP, $\lambda > 350 \text{ nm}$ for LEVO). At the end of illumination, the sample was filtrated with $0.22 \mu\text{m}$ PVDF membrane filters Captiva Econofilter Agilent Technologies (Santa Clara, CA, USA) and HPLC analysis was performed. Moreover, UV–vis spectra have been recorded before and after the irradiation to evaluate the stability of decatungstate in water at pH 6. Two types of control experiments have been carried out: (i) samples containing dissolved decatungstate anion have been kept in the dark and analyzed and (ii) samples not containing sodium decatungstate were irradiated and then analyzed.

2.4. Photocatalytic experiments with heterogeneous $\text{Na}_4\text{W}_{10}\text{O}_{32}$

Increasing amounts of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ were put in the same photoreactor described above and magnetically kept in suspension in aqueous aerated solutions (3 mL, pH 6) containing ATN (10 mg L^{-1}). Irradiation (60 min, $\lambda > 300 \text{ nm}$) was performed with the same Hg medium pressure lamp. Then after centrifugation, filtration and HPLC analysis, the amount of photocatalyst that gave the highest degradation of ATN was considered the optimal and used in all the following experiments.

In a typical photocatalytic experiment, the determined optimal amount of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ was kept in suspension in aqueous solution (3 mL, pH = 6) containing the drug of interest (10 mg L^{-1}) inside a spectrophotometric cell. Then, irradiation was carried out for the required period of time with the selected cut off filter ($\lambda > 300 \text{ nm}$ for ATN and TMP, $\lambda > 350 \text{ nm}$ for LEVO) and then analyzed as described above. Control experiments carried out are listed below: (i) UV–vis spectra of the centrifuged irradiated solutions were recorded to evaluate leaching of decatungstate, (ii)

Table 2
Mobile phase composition employed to analyze the drugs.

Drug	% of ACN	% of phosphate buffer	t_R (min)	λ (nm)
TMP	20	80 (10 mM pH = 3)	4.3	213
LEVO	18	82 (25 mM pH = 4.3)	5.1	292
ATN	5	95 (2 mM pH = 3)	8.3	225

centrifuged solutions have been irradiated to establish eventual activity of traces of decatungstate leached into the solution and (iii) samples containing the drug (10 mg L^{-1}) have been irradiated in the presence of suspended unexchanged silica-gel particles. The amount employed was the same used in the heterogeneous photocatalytic experiments.

Recycle was evaluated by recovering from the reactor the already irradiated amount of photocatalyst, washing it three times with water and drying it at 50°C overnight. Then, it was re-used in an analogous subsequent photocatalytic experiment.

2.5. HPLC analysis

A HPLC/DAD (Waters, MA, USA pump: Waters 515, DAD: Waters PDA 996) was employed under isocratic elution conditions, reported in Table 2. The flow rate was 1 mL min^{-1} , while the column was thermostated at 25°C . The column was $150 \times 4.6 \text{ mm}$ (Phenomenex, CA, USA) and packed with a C18 silica-based stationary phase with a particle diameter of $5 \mu\text{m}$. The injection volume was $20 \mu\text{L}$ for all standards and samples.

2.6. HPLC/MS analysis

HPLC/MS analyses were carried out by means of Surveyor Plus micro-HPLC hyphenated to a linear ion trap mass spectrometer (LTQ XL Thermo Scientific, Waltham, MA, USA). The HPLC apparatus was composed of a solvent delivery system, a quaternary pump (including a membrane degasser) and an autosampler (including a thermostated column compartment). The LTQ system was equipped with an electrospray ionization (ESI) ion source. The mobile phase was obtained as a mixture of ACN and formic acid $0.1\% \text{ v/v}$: water formic acid $0.1\% \text{ v/v}$. Chromatographic separation was performed under gradient elution conditions: 0–6 min 5% ACN, 6–14 min 5–70% ACN, 14–15 min 70% ACN, then held isocratically at 95% of ACN for 3 min before reconditioning the column. The flow rate was $100 \mu\text{L min}^{-1}$, while the column was thermostated at 25°C . The column was $50 \times 2.1 \text{ mm}$ (Restek, Bellefonte, PA, USA) packed with a C18 silica-based stationary phase with a particle diameter of $3 \mu\text{m}$. The injection volume was $5 \mu\text{L}$ for all standards and samples. MS experimental conditions were as follows: spray voltage 4 kV , capillary temperature 275°C , capillary voltage 11 V and tube lens 25 V for positive ESI conditions.

2.7. EPR-spin trapping experiments

EPR-spin trapping experiments were carried out with a Bruker ER200 MRD spectrometer equipped with a TE201 resonator (microwave frequency of 9.4 GHz). The homogeneous samples were aqueous solutions containing 5,5-dimethylpyrroline *N*-oxide (DMPO, $5 \cdot 10^{-2} \text{ M}$) as spin trap and $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \cdot 10^{-4} \text{ M}$). In heterogeneous experiments, silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ was suspended in a solution containing DMPO ($5 \cdot 10^{-2} \text{ M}$) and ATN (10 mg L^{-1}) when requested. The samples were put into a flat quartz cell and directly irradiated in the EPR cavity with a medium pressure mercury lamp equipped with cut off filter ($\lambda > 300 \text{ nm}$). No signals were obtained in the dark and during irradiation of the solution in the absence of decatungstate.

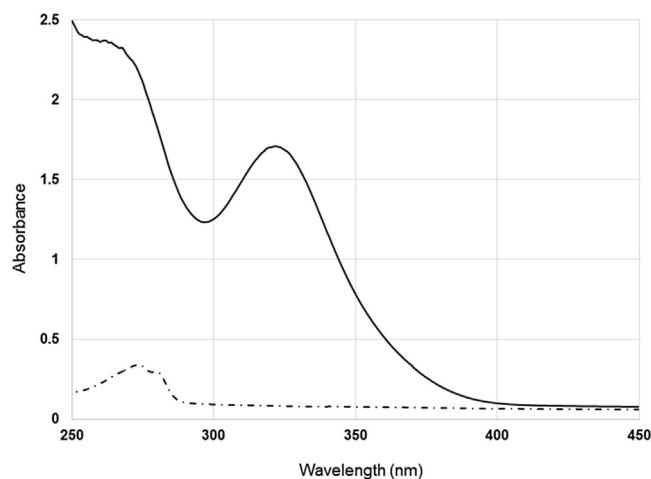


Fig. 1. UV-vis spectra of an aqueous solution containing atenolol (10 mg L^{-1}) in the absence (dashed line) and in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \times 10^{-4} \text{ M}$, solid line).

Table 3
Half time values and kinetic constants determined for drugs concentration decrease upon photoexcitation of $\text{W}_{10}\text{O}_{32}^{4-}$.

Drug	$t_{1/2}$ (min)	k (min^{-1})	R^2
ATN	7.5	0.0924	0.9915
LEVO	38.5	0.0180	0.9866
TMP	53.3	0.0128	0.9882

3. Results and discussion

3.1. Homogeneous photocatalysis

Aqueous solutions ($\text{pH} = 6$) of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \cdot 10^{-4} \text{ M}$) containing the drug of interest (10 mg L^{-1}) have been illuminated using different cut off filters in order to minimize direct photolysis processes (less than 20% of the initial concentration after 120 min irradiation). The proper choice of cut off filter was made as described in the following with ATN as an example: Fig. 1 shows the UV-vis spectrum of an aqueous solution of ATN at the starting concentration (dashed line). When decatungstate is added to the solution (solid line), wavelengths higher than 300 nm are absorbed by the photocatalyst, while the adsorption of ATN is negligible thus minimizing undesired direct photodegradation processes. For this, a cut off filter at $\lambda > 300 \text{ nm}$ was employed in the case of ATN. Following an analogous approach, the same filter has been used with TMP, while in the case of LEVO a cut off filter at wavelengths higher than 350 nm has been employed.

Fig. 2a reports ATN decrease obtained upon decatungstate photoexcitation, expressed as the ratio between the concentration of drug at a certain time (C) and the initial one (C_0), as a function of irradiation time. Control experiments are also reported, in which analogous samples are kept in the dark (empty circles). Fig. 2b and c shows results obtained with LEVO and TMP respectively. Interestingly, ATN is almost completely degraded after 45 min of illumination in the presence of decatungstate, while the decrease in the dark never exceeds 20%, thus confirming an important photocatalytic activity of $\text{W}_{10}\text{O}_{32}^{4-}$. The photocatalytic role of decatungstate is confirmed by results reported in Fig. 2b and c concerning the photodegradation of LEVO and of TMP. More than 80% of the starting drug is disappeared after 120 min and 150 min illumination respectively. Negligible decreases are observed in the dark. Since ratio C/C_0 follows an exponential decay, half-times and kinetic constant values have been estimated and reported in Table 3. The coefficients of determination (R^2) indicate a good fitting of the experimental data to the first law exponential decay

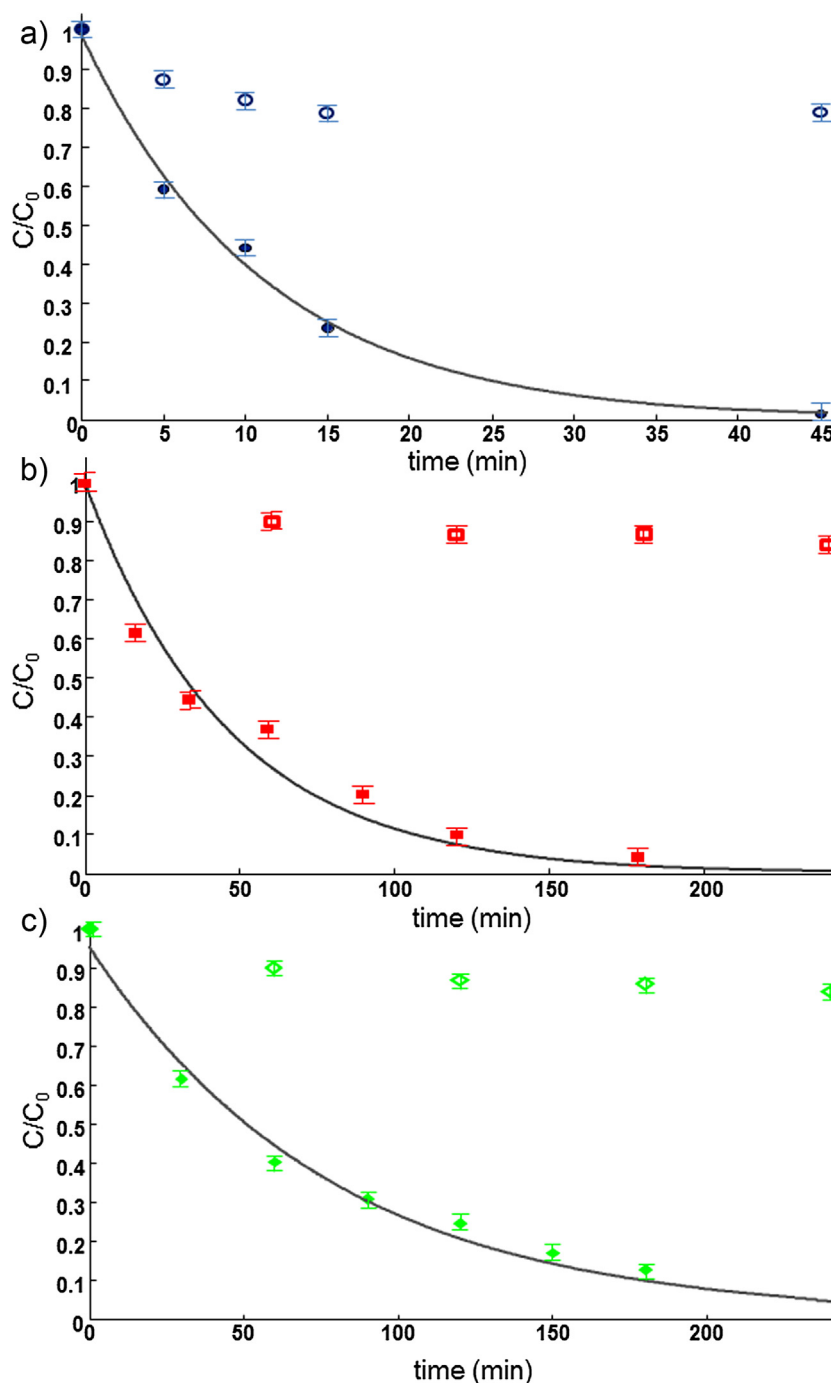


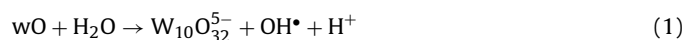
Fig. 2. Degradation kinetics of drugs by photoexcitation of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ (2×10^{-4} M) dissolved in water at pH 6 (full symbols). Control experiments in the dark (empty symbols). $C_0 = 10 \text{ mg L}^{-1}$. (a) ATN, $\lambda > 300 \text{ nm}$; (b) LEVO, $\lambda > 350 \text{ nm}$; (c) TMP, $\lambda > 300 \text{ nm}$.

function, despite the partial degradation of the dissolved photocatalyst. In fact, the decrease of $\text{W}_{10}\text{O}_{32}^{4-}$ is about 35% (see Section 3.4) after 60 min of irradiation. The absorbance at 325 nm decreases from 1.70 to 1.10. In any case, this last value is much more higher than the absorption of the drugs and, during the experiment, the photocatalyst still absorbs the incident photons quantitatively. Moreover, since the $\text{W}_{10}\text{O}_{32}^{4-}$ photoreduction quantum yield reported in literature [41] is about 0.15, the photocatalyst is always in excess to maintain the activity of the degradation cycle (see Scheme 1) without appreciable losses in the kinetics of the process.

3.2. EPR spin trapping investigation

It has been recently demonstrated that photoexcitation of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ dissolved in water leads to the formation of OH^\bullet radicals (Eq. (1)) [28]. Entrapment of these radicals by DMPO gives rise to a quartet ($a_N = a_H = 14.8 \text{ G}$) ascribable to the paramagnetic adduct $[\text{DMPO-OH}]^\bullet$ (Eq. (2)). The addition of ATN, chosen as an example, in the same low concentration (10 mg L^{-1}) employed in the photocatalytic experiments does not affect the formation of $[\text{DMPO-OH}]^\bullet$ adduct. In fact, the quartet (1:2:2:1) is the only detected signal during irradiation (spectrum not shown). This result suggests that

photoexcited decatungstate reacts efficiently with the aqueous solvent (Eq. (1)) and direct oxidation of ATN by the photoreduced polyoxoanion is negligible. Moreover, from EPR spin trapping evidences, we cannot rule out a priori a possible hydrogen atom abstraction from ATN by OH^\bullet radicals. However and interestingly enough, carbon centered radicals of ATN have not been detected during the irradiation, likely suggesting that OH^\bullet radicals initiate ATN degradation following a different pathway, as proposed by Mylonas et al. [42].



3.3. HPLC–MS investigation

The intermediates formed in ATN photocatalytic degradation process were investigated by HPLC–MS. The identifications of the formed breakdown products were based on the analysis of the total ion current (TIC) and on the corresponding mass spectra. The degradation intermediates for ATN are shown in Fig. 3.

The intermediate with 281.1 m/z , corresponds to a ATN derivative in which the original alcohol group is transformed to ketone and aromatic ring has been monohydroxylated [43]. The product with 254.1 m/z may be due to the cleavage of the side isopropyl chain of ATN, while intermediates with 134.1 m/z and 132.1 m/z were identified as an amino-diol and its keto-derivative respectively. Structures similar to those described were observed in the degradation of ATN by photoexcited titanium dioxide [43]. The identification of hydroxylated intermediates of ATN allows us to infer that the main reaction mechanism of OH^\bullet radicals is that of addition to ATN. In fact, its degradation pathway seems to proceed with the initial formation of a monohydroxylated intermediate, which is rapidly converted to its oxidized derivative (281.1 m/z). Successive transformations involve the cleavage of the lateral chain with formation of the compound with a 254.1 m/z and of the species 134.1 and 132.1 m/z . Interestingly, in a previous work it has been reported that the found intermediates are less toxic than the parent molecule [30]. This fact allows us to conclude that the advanced oxidation method based on photoexcited decatungstate seems to not produce toxic oxidation by-products.

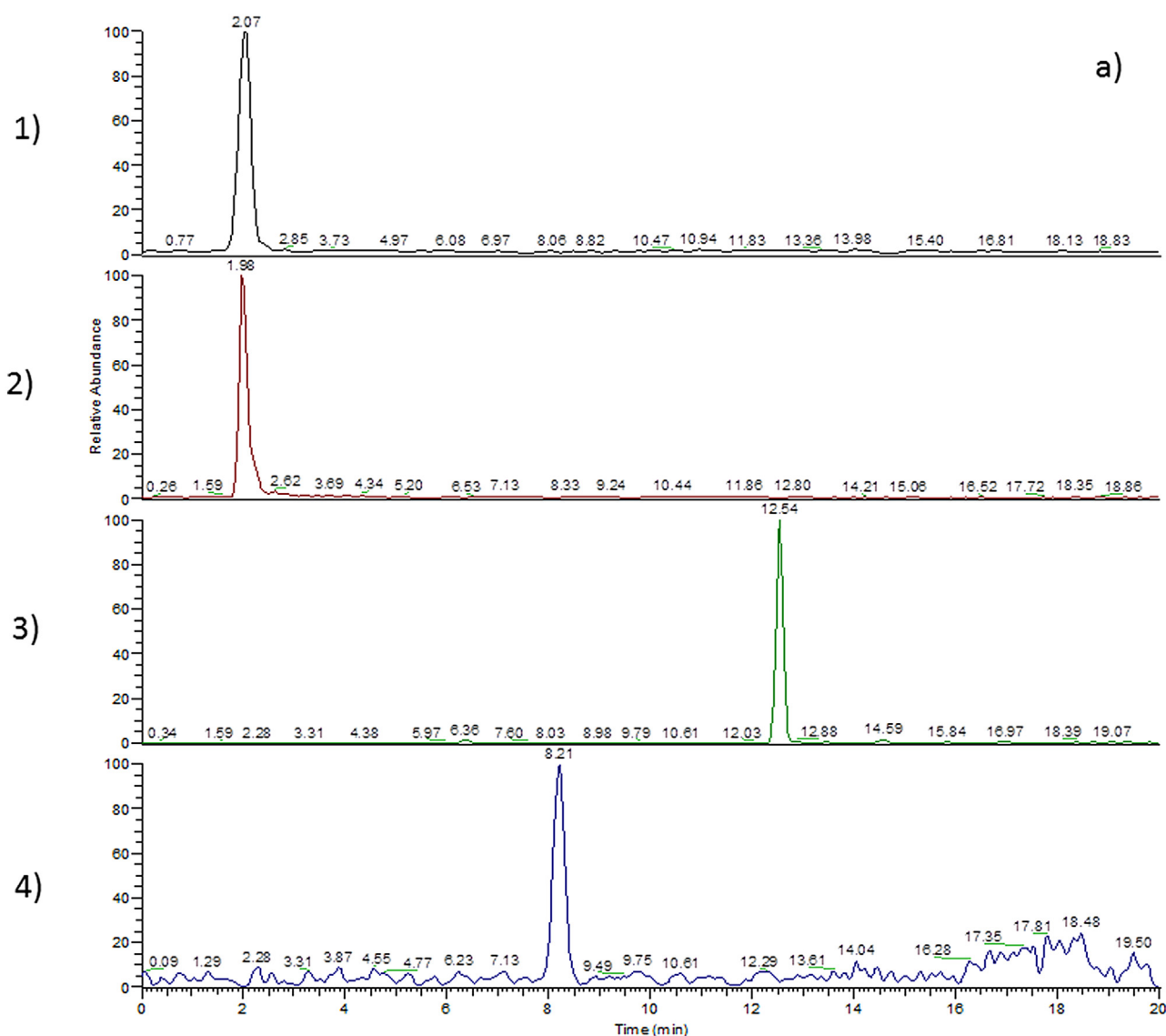


Fig. 3. (a) Chromatograms and relative (b) MS/MS spectra obtained for the intermediates (1) 132 m/z , (2) 134 m/z , (3) 254 m/z and (4) 281 m/z . The elution and detector condition are reported in the HPLC/MS experimental section.

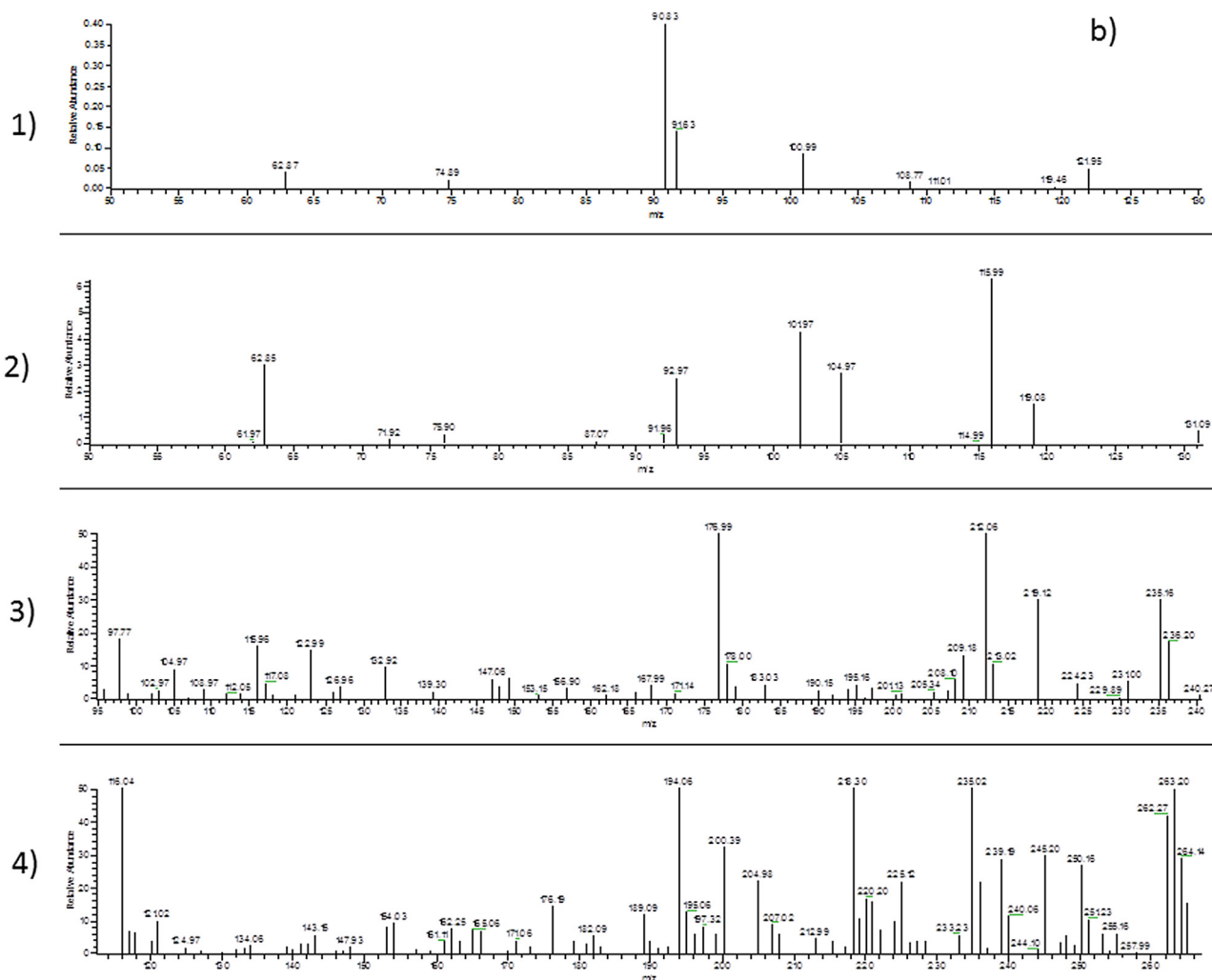


Fig. 3. (Continued)

HPLC–MS results support EPR spin trapping evidences described above. In fact, we observed that OH^\bullet radicals are photo-generated in presence of ATN and no carbon centered radicals are detected. HPLC–MS investigation gives evidence of the addition of OH^\bullet radicals to ATN. Therefore, both techniques independently agree with the fact that drug degradation pathway starts with hydroxylated intermediates formation, excluding other pathways such as hydrogen atom abstraction reaction from ATN by OH^\bullet radicals.

3.4. Heterogenization of sodium decatungstate on functionalized silica particles

Photochemical stability of decatungstate dissolved in water has been estimated. UV–vis spectra of the solution (pH = 6) containing $\text{W}_{10}\text{O}_{32}^{4-}$ have been recorded before and after 60 min irradiation. It is seen a significant absorbance decrease at 325 nm from which we evaluate a degradation of the polyoxoanion of about 35%.

With the purpose of obtaining a more robust photocatalyst, the anionic cluster has been immobilized on silica particles functionalized with $-\text{NH}_2$ groups (see Experimental). For optimizing the slurry amount of photocatalyst with respect to absorption of incident light, some photocatalytic experiments were carried out varying the amount of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ suspended in water. Fig. 4 reports, as an example, the percent of ATN degradation after 1 h irradiation by using increasing amounts of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$.

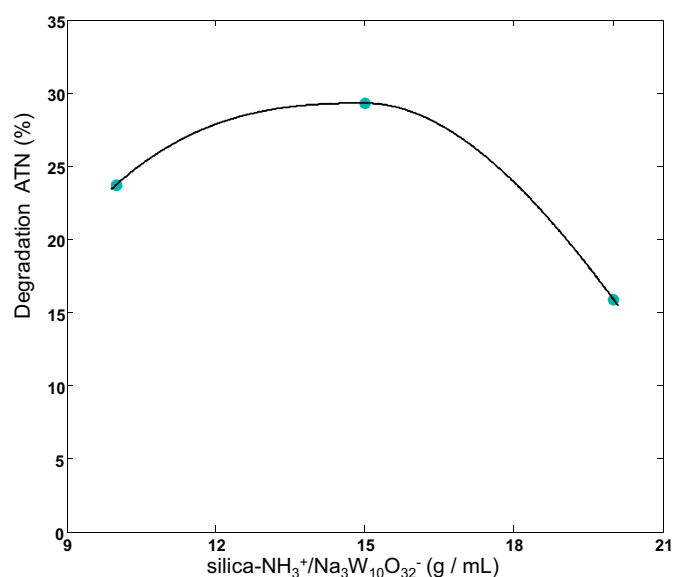


Fig. 4. Percent degradation of ATN vs. amount (expressed as g L^{-1} of solution) of suspended silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ after 1 h irradiation ($\lambda > 300 \text{ nm}$). Reported values are the mean values of three repeated experiments and errors do not exceed $\pm 5\%$.

Table 4

Half time and kinetic constant values determined by drugs concentration decrease upon photoexcitation of silica-NH₃⁺/Na₃W₁₀O₃₂⁻.

Drug	t _{1/2} (min)	k (min ⁻¹)	R ²
ATN	102	0.0068	0.9822
LEVO	94	0.0074	0.9861
TMP	124	0.0056	0.9811

It is seen that the % degradation raises by increasing the amount of the dispersed photocatalyst up to a limit, which corresponds to the maximum amount of illuminated photocatalyst particles. From this plot we evaluated that the optimum amount of silica-NH₃⁺/Na₃W₁₀O₃₂⁻ was 5 g L⁻¹. Throughout this work, we maintained this amount for all the investigated molecules.

3.5. Heterogeneous photo-catalysis

In a typical experiment, silica-NH₃⁺/Na₃W₁₀O₃₂⁻ was suspended in an aqueous solution containing the drug under investigation (10 mg L⁻¹) and then irradiated for the desired time period using the same cut-off filter employed in the homogeneous experiments. Fig. 5 reports the results obtained by irradiation together with those relative to control experiments in the dark. The heterogeneous photocatalyst is active in the degradation of all the investigated drug molecules, although the reaction is slower than that with decatungstate in solution as it can be seen by comparing the kinetics parameters reported in Tables 3 and 4. This behaviour can be ascribed to different factors, such as the illumination conditions, which are usually less homogeneous for suspended powders with respect to dissolved photoactive species. In fact, at a given instant only a part of the supported decatungstate is directly reached by the incident light, and can actively participate to the reaction (see Scheme 1). Moreover, scattering light phenomena could occur, analogously to what described for titanium dioxide

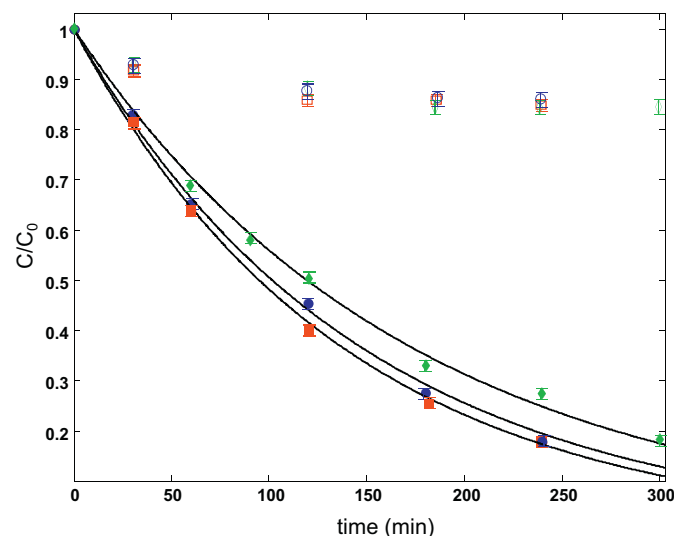


Fig. 5. Degradation kinetics of ATN (●), TMP (◆), LEVO (■) by irradiation of silica-NH₃⁺/Na₃W₁₀O₃₂⁻ (5 g L⁻¹) suspended in solution (3 mL) at pH 6. Control experiments in the dark (empty symbols). C₀ = 10 mg L⁻¹.

suspensions [44]. Finally, mass transfer phenomena, if present, can reduce the reaction velocity of heterogeneous catalysts.

Interestingly, at the end of the irradiation period and after centrifugation, UV spectrum of the illuminated solution did not show the typical spectrum of dissolved decatungstate, indicating that no leaching occurred during the experiment. Moreover, the centrifuged solution has been also illuminated for a second period of time and no further decrease in drug concentration was measured. These control experiments led us to the conclusion that heterogeneous photocatalysis was the process that mainly contributed to ATN degradation.

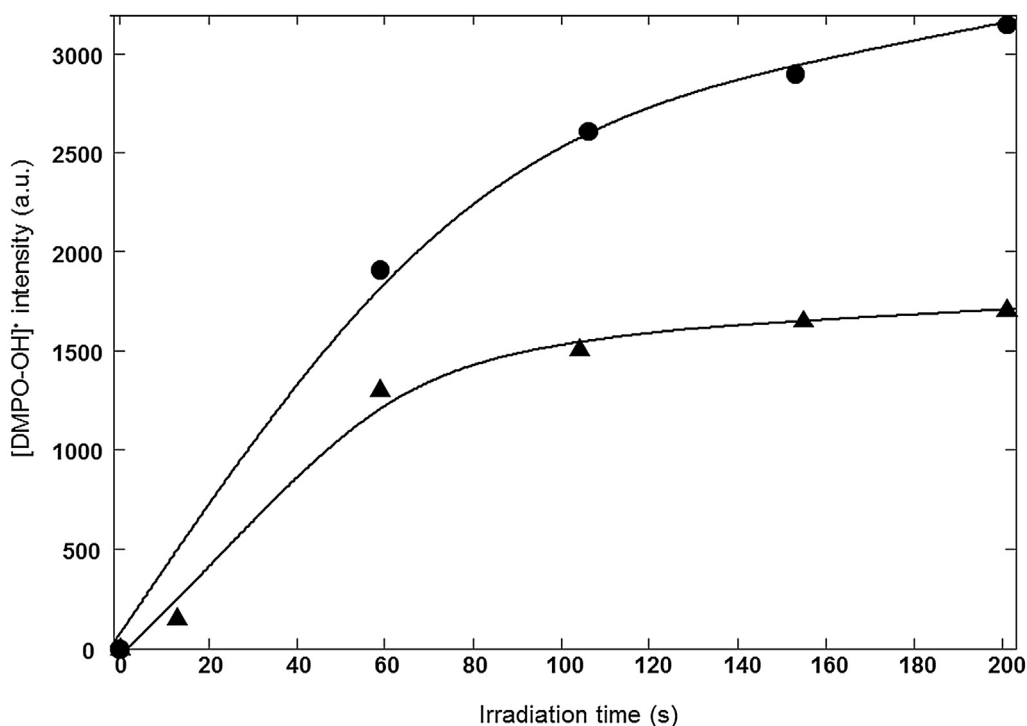


Fig. 6. Fixed-field EPR signal intensity of the [DMPO-OH]• adduct in time upon irradiation ($\lambda > 300$ nm) of silica-NH₃⁺/Na₃W₁₀O₃₂⁻ suspended in an aqueous solution containing DMPO (5×10^{-2} M). ● in the absence of ATN, ▲ in the presence of ATN (10 mg/L).

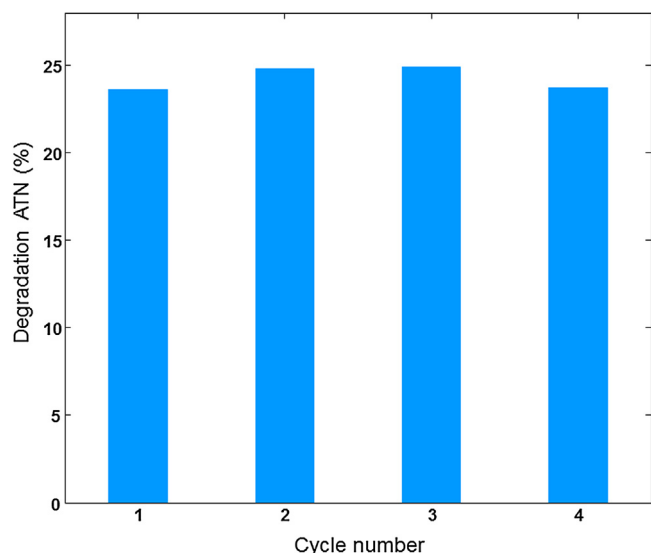


Fig. 7. % ATN degradation obtained irradiating (60', $\lambda > 300$ nm) silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ (5 g L^{-1}) during four consecutive photocatalytic runs.

EPR spin-trapping investigation indicates that heterogenization does not affect the ability of photoexcited $\text{W}_{10}\text{O}_{32}^{4-}$ to produce OH^\bullet radicals. In fact, photoexcitation of aqueous suspensions of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ in the presence of DMPO leads to the formation of the same $[\text{DMPO-OH}]^\bullet$ adduct observed in homogeneous conditions [28].

It has been previously demonstrated that [45], although the trapping process is not quantitative, the amount of trapped radicals can be considered constant if an excess of spin trap is used. On this basis, one can compare spectra intensities obtained under identical experimental conditions and safely assume a proportionality between signal intensity and concentration of photo-generated radicals. For this, we report in Fig. 6 the intensities of $[\text{DMPO-OH}]^\bullet$ adduct during time measured at a fixed field position in absence and in presence of ATN (10 mg L^{-1}).

It is observed that the presence of drug causes a significant decrease of $[\text{DMPO-OH}]^\bullet$ intensity. Likely, this finding can be ascribed to electrostatic interactions between decatungstate anion immobilized on surface particles and ATN, which is mainly in its protonated form at the working pH. Therefore, due to the positive charge, ATN tends to accumulate near the surface where OH^\bullet radicals are produced by photoexcited $\text{W}_{10}\text{O}_{32}^{4-}$. It can be reasonably inferred that this mechanism takes place also for LEVO and TMP, which are in their protonated or zwitterionic form at the working pH too. Interestingly enough, all the studied drugs are photodegraded by the heterogenized decatungstate although their molecular structures are very different each other. This kind of awareness is very important in catalysis [46], and in photocatalysis too, since the characteristics of the solid support allow the design of photoactive sites with favorable properties.

Heterogenization of a soluble photo-catalyst has some important and well-known advantages such as easiness of recover and handling, increase of stability and possibility of recycle without significant loss of activity. Concerning this last point, which is in direct connection with the stability, we evaluated recycle properties by using ATN as a probe. The % degradation of ATN obtained with the regenerated supported heterogeneous photocatalyst for consecutive runs is reported in Fig. 7. We observe that the degradation efficiency is maintained almost constant for 4 cycles of reuse. This result allows us to conclude that the photocatalytic system can be recycled several times without loss of activity, indirectly confirming that leaching of decatungstate is negligible.

4. Conclusions

In this paper a new photocatalytic method for removal of contaminants of emerging concern (i.e. atenolol, levofloxacin, trimethoprim) from water is proposed. Decatungstate anion both in solution and immobilized on modified silica particles is the photoactive species and operates at ambient temperature, atmospheric pressure and at pH values similar to that of natural waters. EPR spin trapping technique demonstrated that drug degradation is mediated by OH^\bullet radicals. HPLC–MS analysis points out the formation of hydroxylated derivative compounds as first intermediates in the overall degradation pathway. The characteristics of the heterogenized photocatalyst favor the interaction between photoactive sites and the drug molecule. Finally, the heterogeneous photocatalyst can be recycled without a significant loss of efficiency thus opening the possibility of developing new solid materials with interesting photocatalytic performance. These results encourage us to continue the research on this subject by considering the effects due to the constituents of typical natural waters (i.e. natural organic matter, carbonate etc.) on the degradation process.

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